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EPR Studies of Axial Ligation of Low-Spin Cobalt(II) Schiff Base Complexes with Lewis Bases and CO

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EPR spectra of cobalt(II) complexes with N_2O_2 type and N_2S_2 type Schiff bases in toluene and/or dichloromethane solution were measured in the absence and presence of Lewis bases and carbon monooxide, CO. The EPR parameters indicate that 4-coordinate $Co(N_2O_2)$ and $Co(N_2S_2)$ complexes have $(d_{x^2-y^2}, d_{xz}, d_{z^2})^6(d_{yz})^1$ and $(d_{x^2-y^2}, d_{xz}, d_{yz})^6(d_{z^2})^1$ ground configuration, respectively, and that 1:1 adducts with Lewis bases and CO have $(d_{x^2-y^2}, d_{xz}, d_{yz})^6(d_{z^2})^1$ ground configuration. The total spin densities are found to fall in the range of 0.65-0.95 for a series of $Co(N_2O_2)$ complexes and 0.50-0.80 for a series of $Co(N_2S_2)$ complexes, respectively, and increase in the order: N-donors>CO>P-donors and $Co(N_2O_2)$>$Co(N_2S_2)$.

KEY WORDS : Cobalt(11) Schiff base / Oxygen-carrying / EPR / Axial ligation / Lewis bases / Electronic structure /

INTRODUCTION

Low-spin cobalt(11) complexes with Schiff bases and porphyrins have received considerably interest because of their ability to form 1:1 complexes with O_2 molecule reversibly.[1-10] Basolo *et al.* reported that several $Co(N_2O_2$-Schiff base) complexes form monomeric oxygen adducts reversibly in the presence of nitrogen donors at a low temperature.[1,2,6] It was also demonstrated that $Co(N_2S_2$-Schiff base) complexes react with O_2 molecule in the presence of Lewis bases at a low temperature.[11-13]

The EPR method is extensively used to study the electronic structure of low-spin cobalt(II) complexes related to the reversible oxygenation.[2,14] EPR results of 4-coordinate cobalt(II) complexes with porphyrins[3,15] and phthalocyanine[16] show that the ground state is $(d_{x^2-y^2}, d_{xz}, d_{yz})^6(d_{z^2})^1$ configuration. For $Co(N_2O_2)$ complexes, there is a controversy over whether the ground state is $(d_{x^2-y^2}, d_{xz}, d_{yz})^6(d_{z^2})^1$[17-19] or $(d_{x^2-y^2}, d_{xz}, d_{z^2})^6(d_{yz})^1$ configuration.[20-22] The EPR results for $Co(N_2S_2)$ complexes are little known. The mono-adducts of cobalt(II) complexes with porphyrins[3,15] and N_2O_2-Schiff bases[18,20] have $(d_{x^2-y^2}, d_{xz}, d_{yz})^6(d_{z^2})^1$ ground configuration. The author found that the mono-adduct of *N, N'*-ethylenebis(monothioacetylacetoneiminato) cobalt(II), Co(tacacen), also has the same ground configuration.[23]

Here the author will report on EPR studies of the axial ligation of *o*-phenylenebis (salicylideneiminato) cobalt(II) ($Co(N_2O_2)$ complex), *N,N'*-ethylenebis(monothiobenzoylacetoneiminato) cobalt(II), *N,N'*-trimethylenebis(monothiobenzoylacetoneiminato) cobalt(II),

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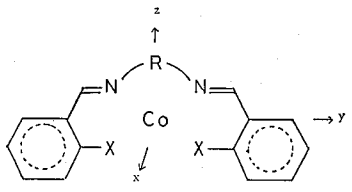
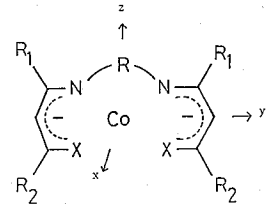


X	R	
O	C_6H_4	*Co*(salphen)
O	$(CH_2)_2$	*Co*(salen)
S	$(CH_2)_2$	*Co*(tsalen)
NH	$(CH_2)_2$	*Co*(amben)



X	R_1	R_2	R	
O	CH_3	CH_3	$(CH_2)_2$	*Co*(acacen)
O	CH_3	C_6H_5	$(CH_2)_2$	*Co*(bzacen)
S	CH_3	CH_3	$(CH_2)_2$	*Co*(tacacen)
S	CH_3	C_6H_5	$(CH_2)_2$	*Co*(tbzacen)
S	CH_3	C_6H_5	$(CH_2)_3$	*Co*(tbzactn)
S	C_6H_5	C_6H_5	$(CH_2)_2$	*Co*(tdbzmen)

and *N*, *N*′-ethylenebis(monothiodibenzoylmethaneiminato) cobalt(II) ($Co(N_2S_2)$ complexes) with Lewis bases and *CO* together with the results for *N*, *N*′-ethylenebis(salicylideneiminato) cobalt(II), *N*, *N*′-ethylenebis(benzoylacetoneiminato) cobalt(II), and *N*, *N*′-ethylenebis(*o*-aminobenzylideneiminato) cobalt(II). All the complexes used in this study except *N*, *N*′-ethylenebis(*o*-aminobenzylideneiminato) cobalt(II) are able to form 1:1 dioxygen adducts with O_2 molecule reversibly in the presence of pyridine at a low temperature.

EXPERIMENTAL

Materials. *The synthesis of ligands.* *N*, *N*′-ethylenebis(salicylideneimine), H_2salen. H_2salen was prepared according to the literature.[24]

N, *N*′-*o*-phenylenebis(salicylideneimine), H_2salphen. Salicylaldehyde (0.2 mol) dissolved in ethanol (50 ml) was added to a suspension of *o*-phenylenediamine (0.1 mol) in ethanol (30 ml), and then ethanol was removed under a reduced pressure. The crude H_2salphen was recrystallized from toluene.

N, *N*′-ethylenebis(benzoylacetoneimine), H_2bzacen, and *N*, *N*′-trimethylenebis(benzoylacetoneimine), H_2bzactn. The ligands were prepared according to the literature.[25]

N, *N*′-ethylenebis(monothiobenzoylacetoneimine), H_2bzacen, and *N*, *N*′-trimethylenebis(monothiobenzoylacetoneimine), H_2bzactn. These ligands were prepared by substitution of the oxygen atoms of H_2bzacen and H_2bzactn to the sulphur atoms according to the literature.[12]

N, *N*′-ethylenebis(monothiodibenzoylmethaneimine), H_2tdbzmen. H_2tdbzmen was prepared from dithiolium salt and ethylenediamine according to the literatures.[27,28]

The synthesis of cobalt(II) complexes. All cobalt(II) complexes were prepared in the nitrogen stream.

N, *N*′-ethylenebis(salicylideneiminato) cobalt(II), *Co*(salen). *Co*(salen) was prepared according to the literature.[24]

N, *N*′-*o*-phenylenebis(salicylideneiminato) cobalt(II), *Co*(salphen). Cobalt acetate tetrahydrate (0.01 mol) was dissolved in methanol (100 ml) and refluxed. H_2salphen (0.01 mol) dissolved in methanol (500 ml) was added and refluxed for 2 hours. After cooling in the ice-bath, *Co*(salphen) was filtered off and washed with methanol and ether.

Table I. Element Analytical Data for the Ligands and Cobalt(II) Complexes

Compound	%C		%H		%N	
	Calcd	Found	Calcd	Found	Calcd	Found
H_2 salen	71.61	71.84	6.02	6.17	10.43	10.42
H_2 salphen	75.93	76.79	5.10	5.01	8.86	8.40
H_2 bzacen(H_2O)	72.01	72.31	7.17	6.97	7.64	8.79
H_2 tbzacen	69.44	69.14	6.37	6.42	7.36	7.31
H_2 tbzactn	70.00	70.20	6.65	6.65	7.10	6.87
H_2 tdbzmen	76.16	75.29	5.58	5.60	5.55	5.58
Co(salen)	59.08	59.17	4.35	4.44	8.61	8.51
Co(salphen) (H_2O)	61.38	61.65	4.12	4.40	7.16	7.41
Co(bzacen)	65.18	65.25	5.48	5.46	6.91	7.18
Co(tbzacen)	60.39	60.66	5.08	5.24	6.40	6.29
Co(tbzactn)	58.02	61.18	5.37	5.32	6.20	5.85
Co(tdbzmen)	68.44	66.90	4.64	4.51	4.99	4.80
Co(amben)	59.82	59.34	4.40	5.05	17.43	17.55

N, *N'*-ethylenebis(benzeylacetoneiminato) cobalt(II), *Co*(bzacen). Cobalt acetate tetrahydrate (0.01 mol) and H_2 bzacen (0.01 mol) were dissolved in methanol (150 ml). The solution was refluxed 1 hour, and cooled in the ice-bath. *Co*(bzacen) was filtered off.

N, *N'*-ethylenebis(monothiobenzoylacetoneiminato) cobalt(II), *Co*(tbzacen), and *N*, *N'*-trimethylenebis(monothiobenzoylacetoneimidato) cobalt(II), *Co*(tbzactn). Cobalt acetate tetrahydrate (0.01 mol) and each ligand (0.01 mol) were dissolved in methanol (100 ml). The solution was warmed for 30 min on a steam bath and then cooled. The complex was filtered off.

N, *N'*-ethylenebis(monothiodibenzoylmthaneiminato) cobalt(II), *Co*(tdbzmen). To a methanol solution (50 ml) of cobalt acetate tetrahydrate (0.005 mol), H_2 tdbzmen (0.005 mol) dissolved in acetone (30 ml) was added. The solution was stirred and condensed at room temperature. The precipitate was filtered off.

N, *N'*-ethylenebis(*o*-aminobenzylideneiminato) cobvlt(II), *Co*(amben). Cobalt acetate tetrahydrate (0.01 mol) and *N*, *N'*-ethylenebis(*o*-aminobenzylideneimine) (0.01mol) was dissolved in methanol (100 mol). The solution was refluxed for 1 hour and then cooled in the ice-bath. The crystals were filtered off.

The ligands and the *Co*(II) complexes prepared were identified by elemental analysis. The results are given in Table I.

N, *N'*-dimethylformamide(*DMF*), pyridine (*Py*), piperidine (*Pipe*), *N*-methylimidazole (*N-MeIm*) and 4-methylpyridine (*MePy*) were purified by distillation, and 4-cyanopyridine (*CNPy*), triphenyl phosphine (PPh_3), tributyl phosphine (PBu_3), trimethyl phosphite ($P(OMe)_3$) and tributyl phosphoshite ($P(OBu)_3$) were used without further purification.

Measurements. All the EPR samples except the *CO* sample were prepared by dissolving *Co*(Schiff base) complexes in dichloromethane and/or toluene containing a proper quantity of the Lewis base. Prior to measurements, the samples were degassed thoroughly. The $Co(N_2S_2)CO$ sample was prepared by exposing a degassed $Co(N_2S_2)$ toluene-dich-

loromethane solution to CO gas for a few hours at room temperature. The EPR spectra were measured with a *JEOL-ME-3X EPR* spectrometer at *X*-band frequencies and calibrated with Mn^{2+} in *MgO* and *DPPH*. The optical spectra were measured with a Hitachi 323 automatic recording spectrophotometer.

Theory for EPR parameters. Assuming that the principal axes of *g*- and *A*-tensors are coincident and the contribution of the quadrupole interaction and the magnetic field-nuclear spin interaction is negligible, the spin-Hamiltonian for low-spin Co^{2+} ion system (d^7, $S=1/2$, and $I=7/2$) is written as follow:

$$\mathcal{H}=\beta(g_{xx}S_xH_x+g_{yy}S_yH_y+g_{zz}S_xH_z)+A_{xx}I_xS_x+A_{yy}I_yS_y+A_{zz}I_zS_z \qquad (1)$$

where β is the Bohr magneton, H_i is the magnetic field. S_i and I_i are the electron and nuclear spin operators, respectively. It can guess instinctively that $3d_{xy}$ orbital is the highest orbital through the inspection of the molecular diagram. Though the order of the other $3d$ orbitals can not be decided, it is well-known that the energy difference between $3d_{xy}$ orbital and the other $3d$ orbital is large.[15] Therefore the wavefunction of the system is described by using d^9 hole configuration.

For $(xy)^2(z^2)^1$ configuration, the following first-order wavefunction are found by taking account of the spin-orbit interaction between the doublet states:

$$\psi^{\pm}=N|(xy)^2(z^2)^{\pm}>+\frac{i\sqrt{3}}{2}b_1|(xy)^2(yz)^{\mp}>\pm\frac{\sqrt{3}}{2}b_2|(xy)^2(xz)^{\mp}> \qquad (2)$$

where $b_1=\xi/\Delta E_{yz}$, $b_2=\xi/\Delta E_{xz}$ and N is the normalized factor. ξ is the effective spin-orbit coupling constant. ΔE_{yz} and ΔE_{xz} are the energy separations for the $(xy)^2(z^2)^1\rightarrow(xy)^2(yz)^1$ and $(xy)^2(z^2)^1\rightarrow(xy)^2(xz)^1$ transitions, respectively. The spin-Hamiltonian parameters are represented as follows because N approximately equals to 1.

$$\begin{aligned} g_{xx}&=2-6b_1\\ g_{yy}&=2-6b_2\\ g_{zz}&=2 \end{aligned} \qquad (3)$$

and

$$\begin{aligned} A_{xx}&=P[-K-2/7-6b_1-3/7b_2]\\ A_{yy}&=P[-K-2/7-6b_2-3/7b_1]\\ A_{zz}&=P[-K+4/7+3/7(b_1+b_2)] \end{aligned} \qquad (4)$$

where $P=g_eg_n\beta\beta_n<\gamma^{-3}>_{3d}$ and $-PK$ is the Fermi contact term.

The first-order wavefunction and the EPR parameters for $(xy)^2(yz)^1$ configuration are obtained by the similar procedure:

$$\begin{aligned} \psi^{\pm}=N|(xy)^2(yz)^{\pm}>&-\frac{i\sqrt{3}}{2}c_1|(xy)^2(z^2)^{\mp}>\pm\frac{i}{2}c_2|(xy)^2(xz)^{\pm}>\\ &-\frac{i}{2}c_3|(xy)^2(x^2-y^2)^{\mp}>\mp\frac{1}{2}c_4(xy)^{\mp}(yz)^2> \end{aligned} \qquad (5)$$

$$\begin{aligned} g_{xx}&=2-6c_1-2c_3\\ g_{yy}&=2-2c_4\\ g_{zz}&=2-2c_2 \end{aligned} \qquad (6)$$

and

$$A_{xx}=P[-K-4/7-6c_1-2c_3-3/7(c_2+c_4)]$$

$$A_{yy}=P[-K+2/7-2c_4+3/7(c_1+c_2-c_3)]$$
$$A_{zz}=P[-K+2/7-2c_2+3/7(c_3-c_1-c_4)] \quad (7)$$

where $c_1=\xi/\Delta E_{z^2}$, $c_2=\xi/\Delta E_{xz}$, $c_3=\xi/\Delta E_{x^2-y^2}$, and $c_4=\xi/\Delta E_{xy}$. ΔE_{z^2}, ΔE_{xz}, ΔE_{xy}, and $\Delta E_{x^2-y^2}$ are the energy separations between $(xy)^2(yz)^1$ state and $(xy)^2(z^2)^1$, $(xy)^2(xz)^1$, $(xy)^1(yz)^2$, and $(xy)^2(x^2-y^2)^1$ states, respectively. The representation of g- and A-tensors of the other configurations is omitted because it is found that the ground configuration of *Co* (II) complexes in this study is either $(xy)^2(yz)^1$ or $(xy)^2(z^2)^1$ configuration.

RESULTS AND DISCUSSION

4-coordinate complexes. EPR and optical spectra of *Co*(tbzacen) and *Co*(bzacacen) are shown in Figs. 1-4. EPR parameters of $Co(N_2S_2)$ and $Co(N_2O_2)$ complexes are tabulated in Table II. It is found that both $Co(N_2O_2)$ and $Co(N_2S_2)$ complexes have

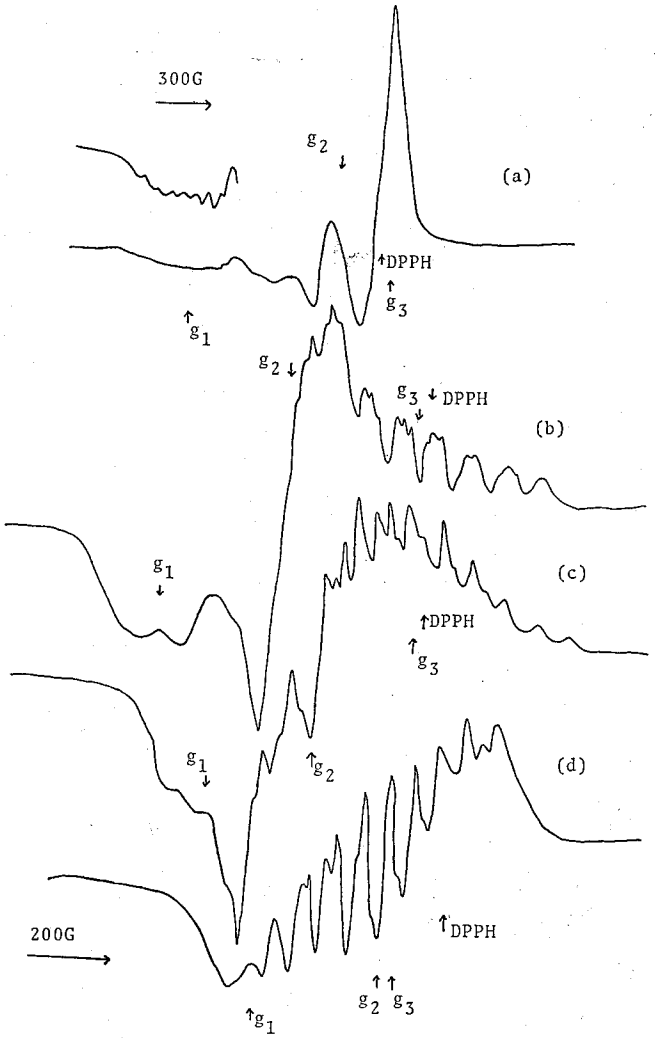


Fig. 1. EPR spectra of *Co*(tbzacen) in dichloromethane-toluene frozen solution at 77K. (a) 10% DMF, (b) 10% pyridine, (c) 1M PPh_3, (d) *CO* (650 Torr).

characteristically large g_1 and A_1 values, and commonly $g_3<g_e$ value. Considering the g expressions for various configurations for the result observed for Co(bzacen), the relationship of $g_3\leq g_e$ is found in the g_{xx} for $(xy)^2(z^2)^1$ and g_{yy} for $(xy)^2(yz)^1$ configuration. These configurations imply that the other g values are larger than g_e. Solving the equations (3) and (4) for $(xy)^2(z^2)^1$ configuration, it is found that $P=0.0150$ cm^{-1} and $K=0.184$ when $A_{xx}=104.4\times10^{-4}$cm^{-1} and $A_{zz}=45.6\times10^{-4}$cm^{-1}. A_{yy} value calculated by using these P and K values is -54.5×10^{-4}cm^{-1}. This A_{yy} value is consistent with $|A_2|$ value observed. On the other hand, solving the Eqs. (6) and (7) for $(xy)^2(yz)^1$ configuration., it is found that $P=0.0185$ and $K=-0.027$ when $A_{xx}=104.4\times10^{-4}$cm^{-1}, $A_{zz}=47.2\times10^{-4}$ cm^{-1} and $A_{yy}=45.6\times10^{-4}$cm^{-1}.

P values found in both configurations are smaller than free Co^{2+} ion value ($P_0=0.0254$ cm^{-1}).[29] This reduction of P value occurs due to the covalency between Co^{2+} ion and N_2O_2 ligand. The effective spin-orbit coupling constant $\xi(=(Z_{eff}e^2/2m^2c^2)\langle\gamma^{-3}\rangle)$. also reduces due to the covalent bond. It seems reasonable that P and ξ assume the reduction by the same degree since these are dependent on $\langle\gamma^{-3}\rangle$. The relationship,

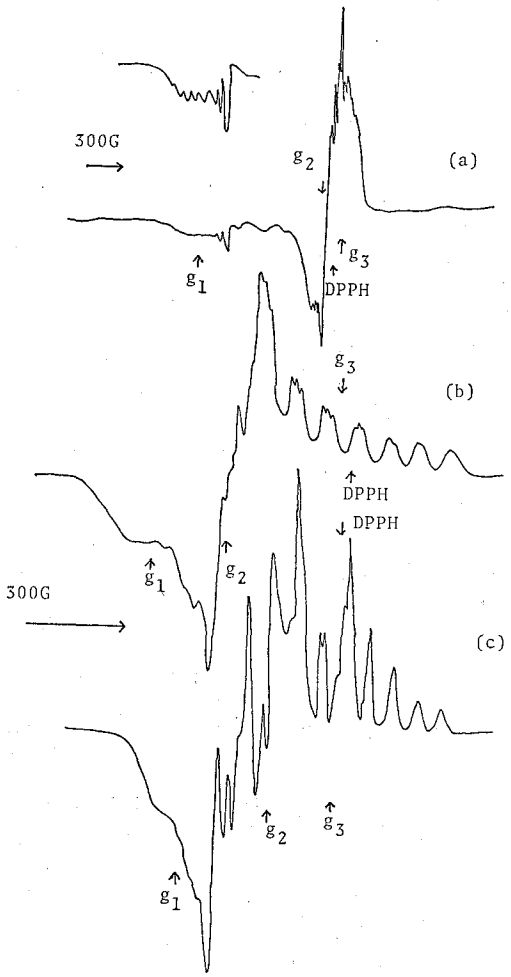


Fig. 2. EPR spectra of Co(bzacen) in dichloromethane-tolune frozen solution at 77K. (a) 10% DMF, (b) 10% pyridine, (c) 1M PPh_3.

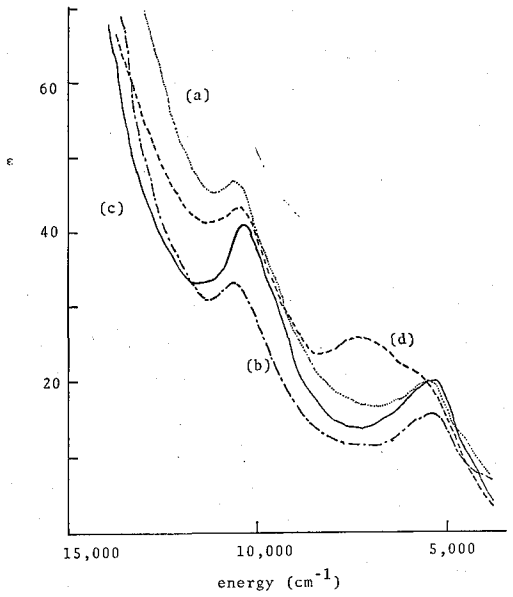


Fig. 3. Absorption spectra of *Co*(tbzacen) in $CHCl_3$ solution (a) none (b) 10% pyridine (c) 0.25 mol/dm^3 PPh_3 (d) 10% $P(OMe)_3$

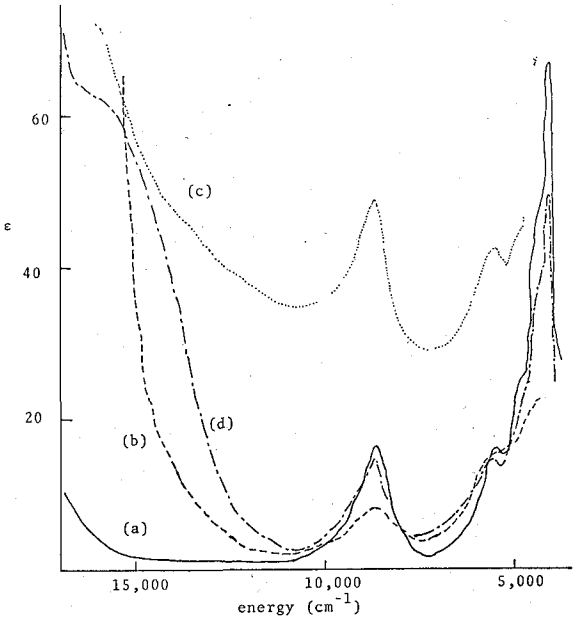


Fig. 4. Absorption spectra of *Co*(bzacen) in $CHCl_3$ solution (a) none (b) 50% pyridine (c) 0.25 mol/dm^3 PPh_3 (d) 10% $P(OMe)_3$

$\xi/\xi_0=P/P_0$, is obtained. ΔE value can be estimated by utilizing this relationship and the g equations. For *Co*(bzacen) with $(xy)^2(z^2)^1$ ground configuration ΔE_{xz} and ΔE_{yz} calculated are 82, 900 cm^{-1} and 1, 560 cm^{-1}, respectively. For $(xy)^2(yz)^1$ ground configuration ΔE_{xz}, ΔE_{z^2}, $\Delta E_{x^2-y^2}$, and ΔE_{xy} calculated are 34, 000 cm^{-1}, 2, 080 cm^{-1}, 8, 700 cm^{-1}, and 24, 900 cm^{-1}, respectively.

Table II. EPR Parameters for Co(Schiff Base) Complexes

(I) $(xy)^2(yz)^1$ ground state

Complex	g_{xx}	g_{yy}	g_{zz}	A_{xx}	A_{yy}	A_{zz}	ΔE_{xz}	ΔE_{xy}	$\Delta E_{x^2-y^2}$	ΔE_{z^2}	P	K	ref
Co(salen)	3.322	1.916	2.017	151.6	38.9	61.4	57.0	9.67	8.4	2.04	0.0205	−0.027	
Co(salphen)	3.845	1.73	1.75	290	40	24	3.88	3.59	8.4	1.48	0.0239	−0.054	14
Co(bzacen)	3.168	1.972	2.024	104.4	45.6	47.2	34.0	24.9	8.7	2.08	0.0184	−0.027	
Co(acacen)	3.26	1.88	2.00	115.8	37.5	34.0	8.0	5.0	57.0	1.7	0.0186	0.126	22
	3.190	1.925	2.01	115	31	37	120.0	12.44	8.4	2.68	0.0236	0.241	14
Co(amben)	2.662	1.976	2.049	−7.1	30.1	24.4	10.74	19.38	6.25	2.04	0.0124	0.150	

(II) $(xy)^2(z^2)^1$ ground state

Complex	g_{xx}	g_{yy}	g_{zz}	A_{xx}	$-A_{yy}$	A_{zz}	ΔE_{xz}	ΔE_{yz}	P	K	ref
Co(tacacen)	3.210	2.182	1.978	113.4	27.9	44.9	10.00	1.49	0.0148	0.1691	
Co(tbzacen)	3.023	2.215	1.978	92.7	40.6	48.9	10.60	2.20	0.0185	0.220	
Co(tbzactn)	2.690	2.157	2.002	7.1	35.0	16.3	7.35	1.64	0.0089	0.332	
Co(tdbzmen)	2.800	2.195	1.992	101.0	11.7	96.9	10.00	2.42	0.0159	−0.109	
Co(acacen)	3.26	1.88	2.00	115.8	37.5	34.5	8.0	1.9	0.0175	0.28	22

A: $10^{-4}cm^{-1}$, ΔE: 10^3cm^{-1}, P: cm^{-1}.

It is difficult to determine whether the ground state of Co(bzacen) is $(xy)^2(z^2)^1$ or $(xy)^2(yz)^1$ ground configuration. Cariati *et al.* reported the EPR spectrum of Co(acacen) single crystal diluted in Ni(acacen)[22]. The results are tabulated in Table II. They found that EPR parameters and ΔE values are fit for the theoretical expressions when $g_{yy}=1.88$ in $(xy)^2(z^2)^1$ ground configuration. But this fit is questionable because g expressions of $(xy)^2(z^2)$ configuration predict $g_{yy}>g_e$ when $g_{zz}=2.00$. It is found that P value is less than ~ 0.0100 cm^{-1} when $\Delta E_{xz}=8,000$ cm^{-1} in terms of $\xi/\xi_0=P/P_0$, though they find that EPR parameters and ΔE values fit the theoretical expressions of $(xy)^2(yz)^1$ configuration when $\Delta E_{xz}=8,000$ cm^{-1}. Solving the theoretical expressions for Co(acacen)[14,22], the best fit with EPR parameters and ΔE is obtained when the ground configuration is $(xy)^2(yz)^1$ configuration. This suggests that Co(bzacen) also has $(xy)^2(yz)^1$ ground configuration because of the similarity of the structure of Co(acacen) and Co(bzacen). It is found that the other $Co(N_2O_2)$ complexes have $(xy)^2(yz)^1$ ground configuration by the same procedure, though the results of the powder samples of Co(salen)[17] and Co(salphen)[14] are not satisfactory since g_{yy} and g_{zz} are less than g_e.

EPR spectrum of Co(tbzacen) is similar to that of Co(bzacen). Solving the g and A equations for various configurations by the same procedure as $Co(N_2O_2)$ complexes, a best fit between EPR parameters and ΔE and the theoretical expressions is obtained when the ground configuration for Co(tbzacen) is $(xy)^2(z^2)^1$ configuration. It is found that the other $Co(N_2S_2)$ complexes have $(xy)^2(z^2)^1$ ground configuration by the same treatment though a large A_{zz} value is estimated for Co(tdbzmen).

ΔE calculated from EPR parameters indicates the relative levels of the states. The relative energy diagrams of $Co(N_2O_2)$ and $Co(N_2S_2)$ complexes are shown in Fig. 5. For $Co(N_2O_2)$ complexes ΔE_{xz} shows that $(xy)^2(xz)^1$ configuration is the most stable state. $\Delta E_{x^2-y^2}$ indicates that the characteristic band of $Co(N_2O_2)$ complexes at about 8,000 cm^{-1} is $(xy)^2(yz)^1\rightarrow(xy)^2(x^2-y^2)^1$ transition. For $Co(N_2S_2)$ complexes ΔE_{xz} shows that the

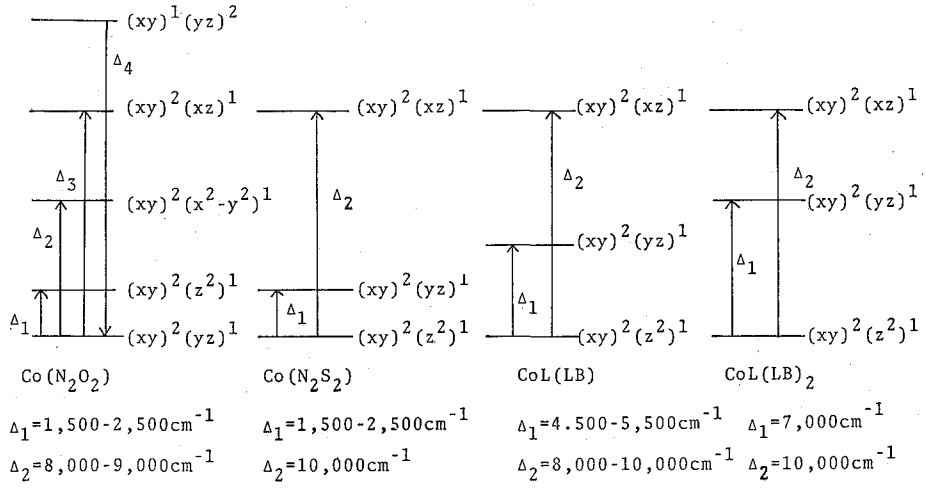


Fig. 5. The relative energy diagrams of $Co(N_2O_2)$, $Co(N_2S_2)$, monoand bis adducts.

common band of $Co(N_2S_2)$ complexes except Co(tbzactn) at 10,000 cm^{-1} is the transition between $(xy)^2(z^2)^1$ and $(xy)^2(xz)^1$ states. It expects that $Co3d_{yz}$ orbital is stabilized higher than $3d_{z^2}$ orbital by $Cod_\pi(3d_{xz}, 3d_{yz})-Sd_\pi$ back bonding. The difference of the assignment of the absorption band at 8,000~10,000 cm^{-1} for $Co(N_2O_2)$ and $Co(N_2S_2)$ complexes is probably due to $d_\pi-d_\pi$ interaction. It is found that $(xy)^2(yz)^1$ and $(xy)^2(z^2)^1$ states exist very closely for both complexes. This suggests that the large g_{xx} and A_{xx} values are produced due to the small energy difference between the two states.

EPR spectra of 5-coordinate complexes. Typical EPR spectra of Co(tbzacen) with pyridine, triphenyphosphine and CO are shown in Fig. 1 for example. The EPR parameters are tabulated in Table III. The nitrogen-14 ($I=1$) superhyperfine structure splitting into a triplet appears in the EPR spectrum for the $Co(N_2S_2)$-pyridine systems. This indicates that the $Co(N_2S_2)$ complexes form 5-coordinate $Co(N_2S_2)$ (pyridine) adducts with one pyridine molecule. The phosphorus-31 ($I=1/2$) superhyperfine splitting similarly demonstrates that one triphenylphosphine molecule coordinates to the $Co(N_2S_2)$ complexes. The author measured the EPR spectra of $Co(N_2S_2)$ solutions containing the higher concentration of Lewis bases. However, no evidence for a formation of $Co(N_2S_2)(LB)_2$ bis adducts was obtained. The CO adduct is obtained by exposing a $Co(N_2S_2)$ complex solution to CO gas. It, however, is not formed in the presence of Lewis bases, though Drago *et al.*[30] demonstrated the formation of 6-coordinate $Co(salMeDPT)CO$ complex which is prepared from CO gas and 5-coordinate bis(salicylidene-γ-iminopropyl) methylaminocobalt(II) complex, $Co(salMeDPT)$.

The EPR spectra of Co(bzacen) with Lewis bases show the same behavior as $Co(N_2S_2)$ complexes. However, Co(salen) and Co(salphen) form the 5-coordinate complexes with DMF and the bis adducts in the high concentration of pyridine. These EPR parameters are given in Table IV.

In most cases, EPR parameters of mono and bis adducts have the order of $|A_3|$, $|A_2|>|A_1|$ when $g_1>g_2>g_3$. This indicates that mono and bis adducts have a common ground state. The presence of hyperfine interaction with bound nitrogen or phosphorus

Table III. EPR Parameters for Co(N_2S_2-Schiff Base) (LB) Complexes

	LB	g_{xx}	g_{yy}	g_{zz}	A_{xx}	$-A_{yy}$	A_{zz}	A_Z^{LB}	ΔE_{xz}	ΔE_{yz}	P	K	ref
(I)	Co(tbzacen)												
	Py	2.462	2.214	2.006	10.6	36.4	77.0	16.3	10.5	4.8	0.0182	0.100	
	MePy	2.468	2.221	2.007	5.0	44.8	72.5	16.1	10.5	4.9	0.0188	0.138	
	Pipe	2.476	2.220	2.008	15.1	36.3	80.6	16.1	10.5	4.8	0.2187	0.092	
	N-MeIm	5.448	2.231	2.009	0.7	46.5	74.0	16.3	10.5	5.4	0.0197	0.147	
	PPh_3	2.347	2.167	2.024	−5.0	14.5	73.1	190	10.3	4.9	0.0140	0.008	
	PBu_3	2.332	2.156	2.009	−3.6	28.1	62.1	144	10.3	4.8	0.0310	0.060	
	$P(OMe)_3$	2.397	2.150	1.996	4.8	28.4	59.1	201	10.3	3.9	0.0125	0.061	
	$P(OBu)_3$	2.402	2.161	2.002	0.3	33.4	58.0	202	10.3	4.1	0.0135	0.101	
	CO	2.275	2.039	2.018	−23.6	56.3	59.7		49.0	6.6	0.0149	0.149	
(II)	Co(tbzactn)												
	Py	2.498	2.247	2.014	29.5	5.4	72.9	12.2	7.4	3.7	0.0149	0.031	
	N-MeIm	2.462	2.248	2.024	21.6	8.2	70.9	12.2	7.4	4.0	0.0150	0.048	
	(Pipe)	2.665	2.150	2.001	5.0	34.9	16.2		7.4	1.6	0.0089	0.332	
(III)	Co(tdbzmen)												
	Py	2.436	2.223	2.010	9.7	26.3	75.1	16.0	10.0	5.1	0.0182	0.111	
	PPh_3	2.369	2.162	2.019	10.0	15.3	68.0	164	10.0	4.4	0.0132	0.017	
	$P(OBu)_3$	2.369	2.143	1.983	9.2	15.1	60.4	160	10.0	3.8	0.0116	0.014	
	CO	2.326	2.080	2.025	−1.6	43.0	42.7		18.4	4.4	0.0118	0.180	
(IV)	Co(tacacen)												
	Py	2.444	2.207	1.993	16.2	21.6	77.2	15.3	10.2	5.1	0.0173	0.077	23
	CO	2.290	2.070	2.029	−25.6	58.7	62.0		28.4	6.7	0.0162	0.165	23
(V)	Co(tsalen)												
	Py	2.44	2.20	2.033	21.0	10.0	72.0	16.0	8.7	4.0	0.0143	0.022	11

A: $10^{-4}cm^{-1}$, ΔE: 10^3cm^{-1}, P: cm^{-1}

Table IV. EPR Parameters for Co(N_2O_2-Schiff Base) (LB) Complexes

	LB	g_{xx}	g_{yy}	g_{zz}	A_{xx}	$-A_{yy}$	A_{zz}	A_Z^{LB}	ΔE_{xz}	ΔE_{yz}	P	K	ref
(I)	Co(bzacen)												
	Py	2.467	2.260	2.017	12.5	35.1	89.6	14.2	8.7	5.6	0.0215	0.102	
	N-MeIm	2.440	2.259	2.019	6.8	34.6	89.7	15.1	8.7	5.9	0.0214	0.102	
	Pipe	2.504	2.263	2.023	18.3	37.8	87.6	13.6	8.7	5.3	0.0217	0.113	
	CNPy	2.499	2.268	2.027	22.8	31.9	94.6	14.4	8.7	5.4	0.0221	0.089	
	PPh_3	2.416	2.175	2.020	−0.1	49.1	78.5	178	8.7	5.6	0.0190	0.116	
(II)	Co(salen)												
	DMF	2.444	2.278	2.010	29.4	1.1	97.3	15.4	8.7	5.4	0.0197	0.027	
	Py	2.41	2.24	2.012	22.7	5.4	90.8	15.1	9.0	5.3	0.0178	0.014	20
	Py_2	2.354	2.270	2.028	−10.6	26.1	77.0	12.0	9.0	6.9	0.0198	0.135	4
	CO	2.28	2.17	2.02	14	35	80.2		14.2	8.7	0.0179	0.090	7
(III)	Co(salphen)												
	DMF	2.431	2.273	2.030	38.8	−3.7	105.2		10.0	5.2	0.0187	−0.055	
	Py	2.407	2.226	2.012	32.0	10.0	91.0	16.5	10.0	5.5	0.0184	0.032	14
	Py_2	2.305	2.196	2.035	−17.9	35.1	72.0	12.5	10.0	7.1	0.0192	0.154	
	PPh_3	2.367	2.196	2.019	12.1	13.2	81.9	187	10.0	5.3	0.0159	0.017	
(IV)	Co(acacen)												
	Py	2.435	2.226	2.012	30.8	8.8	86.7	14.0	8.4	4.4	0.0155	−0.036	10

A: $10^{-4}cm^{-1}$, ΔE: 10^3cm^{-1}, P: cm^{-1}

atom implies that the Lewis base coordinates to the axial direction and that an unpaired electron is in an orbital with large component in this direction (d_{xz}, d_{yz} or d_{z^2}).

Maki's equations[31] by the same procedure as 4-coordinate complexes are utilized to determine the ground state of mono and bis adducts studied. The g_3 value in the *Co*(tbzacen)(pyridine) complex is nearly the free electron g value ($g_e=2.0023$). Maki's equations predict that g_{zz} expression for $(xy)^2(z^2)^1$ configuration in various configurations is g_e. g_{xx} and g_{yy} are larger than g_e. This trend is consistent with g_1 and g_2 observed. Therefore, the z direction is identified with the principal axis having g_3 value close to 2.0023. The other direction can not be determined. Solving the Eqs. (3) and (4) by the similar procedure for 4-coordinate complexes, the ground configuration of *Co*(tbzacen)(pyridine) complex is fit for $(xy)^2(z^2)^1$ configuration when $g_1=g_{xx}$, $g_2=g_{yy}$, and $A_3=A_{zz}>0$, and $\Delta E_{xz}=10,500\ \mathrm{cm}^{-1}$. It seems that ΔE_{yz} value calculated ($4,800\ \mathrm{cm}^{-1}$) is consistent with the observed band in $CHCl_3$ at $5,500\ \mathrm{cm}^{-1}$ as tabulated in Table III. This suggests that the ground configuration of *Co*(tbzacen)(pyridine) is $(xy)^2(z^2)^1$ configuration. For the other mono and bis adducts of *Co*(N_2S_2) and *Co*(N_2O_2) complxes it is found that the ground configuration is $(xy)^2(z^2)^1$ configuration by the same procedure as *Co*(tbzacen)(pyridine).

McGarvey[32] has extended the theory for the spin-Hamiltonian parameters of low-spin *Co*(II) complexes to third order perturbation, including the effects of admixture of excited quartet states with the ground doublet state. Because the symmetry of the 1:1 adducts is no higher than C_{2v}, mixing $d_{x^2-y^2}$ to d_{z^2} orbital is symmetry allowed. Including this admixture, McGarvey obtains

$$g_{zz}=g_e+2/3(c_3^2+c_4^2+c_3c_4+(3a^2-b^2)c_1c_2 -[(3a)^{1/2}+b]^2c_2^2-[(3a)^{1/2}-b]^2c_1^2-8b^2c_6^2$$

where $c_1=\xi/\Delta(^2B_1)$, $c_2=\xi/\Delta(^2B_2)$, $c_3=\xi/\Delta(^4B_1)$, $c_4=\xi/\Delta(^4B_2)$, $c_6=\xi/\Delta(^2A_2)$, and the unpaired electron is in $(a\ d_{z^2}+b\ d_{x^2-y^2})$ orbital. $^2B_1$, $^2B_2$ and $^2A_2$ excited doublet states are $(xy)^2(xz)^1$, $(xy)^2(yz)^1$, and $(xy)^1(z^2)^2$ states, respectively. The quartet states $^4B_1$ and $^4B_2$ correspond to the $(z^2)^1(yz)^1(xy)^1$ and $(xz)^1(z^2)^1(xy)^1$ states, Δ is the energy difference between the excited and ground state. ξ is the spin-orbit coupling constant of *Co*(II).

If quartet states do not mix to ground state, $c_3=c_4=0$, g_{zz} is expected to be less than g_e for any value of $b(0\leqq b\leqq 1)$. Since in most cases g_{zz} values are greater than g_e, the contribution of the excited quartet states to the ground state are not negligible.

Lin suggests that $^4B_1$, and $^4B_2$ states lie close to the ground state in *Co*(porphyrins)-(*LB*) complexes.[15] McGarvey has produced the same conclusion for 4-coordinate *Co*(bzacen).[19] However, the ground state was reasonably determined by applying the Maki's equations to the mono and bis adducts studied with $g_{zz}>g_e$. It seems significantly meaningful that the Maki's expressions are applied to determine the ground state in spite of neglecting the excited quartet states.

The relative energy diagrams for the mono and bis adducts are shown in Fig. 5. The energy difference between $(xy)^2(yz)^1$ excited doublet state and $(xy)^2(z^2)^1$ ground doublet state increases as the axial ligand coordinates to the 4-coordinate complexes. This implies that d_{z^2} orbital is destabilized due to the coordination of the axial ligand.

EPR spectrum of *Co*(amben), analogous to *Co*(salen) showed the specific behavior. EPR spectrum of *Co*(amben) with pyridine is completely the same spectrum as 4-coordinate *Co*(amben) complex. This indicates that *Co*(amben) did not react with

Lewis base. Green *et al.*[33] suggests that the unpaired electron is in the in-plane orbital based on considering the reaction with Lewis bases, and propose that the ground state is a $(xy)^2(x^2-y^2)^1$ configuration. Urbach *et al.*[21] reported that ground state is a $(xy)^2(z^2)^1$ configuration for optical-active, *N, N'*-bis(*o*-aminobenzylidene)-(*R*)-(−)-propane-1, 2-diaminocobalt(II), $Co(aba)_2(-)pn$, analogous to *Co*(amben). Solving the *g* and *A* expressions for various configurations by the similar procedure, it is found that the ground state of *Co*(amben) is a $(xy)^2(yz)^1$ configuration. Then the data of C. D. and optical spectra for $Co(aba)_2(-)pn$ was utilized to solve the *g* and *A* equations. It is estimated that $\Delta E_{x^2-y^2}$ of *Co*(amben) is smaller than that of $Co(N_2O_2)$ complexes. This indicates that the admixture of $d_{x^2-y^2}$ orbital with d_{yz} orbital caused by the spin-orbit interaction is strong. It is supposed that the delocalization of an unpaired electron into the in-plane orbital weakens the reactivity with pyridine in the axial position.

Cobalt-59 spin densities. Cobalt-59 spin densities can be evaluated from the EPR parameters. Cobalt 3*d* spin densities (ρ_{3d}) are estimated by comparing the observed dipolar constant with the theoretical value according to the equation: $\rho_{3d}=[(A_d)_{obsd}]/[(A_d)_{theor}]=\rho/\rho_0$ where $\rho_0=0.0254$ cm.$^{-1}$

Cobalt 4*s* spin densities (ρ_{4s}) are determined from the relationship $A_{contact}=-PK=\rho_{4s}[A(Co4s)]+\rho_{3d}[A(Co3d)]$, where $A(Co4s)=0.1232$ cm^{-1} and $A(Co3d)=-0.00840$ cm^{-1}.[34] The results for cobalt-59 spin densities are given in Tables V-VII.

The total cobalt spin densities for the axial ligands increase in the order: *N*-donors $>CO>$ *P*-donors. The unpaired spin becomes delocalized as the covalency increases. This suggests that the covalency between $Co3d_{z^2}$ and ligand σ-orbital reduces according to this order. The total spin densities for the equatorial ligands are $Co(N_2O_2)>Co(N_2S_2)$ complexes. This indicates the delocalization of the unpaired spin by $Cod_\pi-Sd_\pi$ back donation. This tendency of the cobalt spin densities is consistent with that of the oxygenation ability of the $Co(N_2O_2)$ and $Co(N_2S_2)$ complexes.[6,13] This implies that the oxygenation of cobalt(II) complexes occurs easily as the axial ligand increases the spin densities on the central Co^{2+} ion.

Table V. Cobalt-59 Spin Densities for Co(Schiff Base) Complexes

Complex	PK	A_d	ρ_{3d}	ρ_{4s}	ρ_{Co}	%4s
Co(salen)	−5.1	117.4	0.809	0.059	0.868	6.82
Co(salphen)	−12.9	136.6	0.941	0.075	1.016	7.35
Co(bzacen)	−5.0	105.4	0.726	0.054	0.780	6.92
Co(acacen)	48.4	106.3	0.732	0.011	0.743	1.48
	56.9	134.9	0.929	0.017	0.946	1.82
Co(amben)	18.6	71.0	0.489	0.018	0.508	3.60
Co(tacacen)	25.0	84.6	0.583	0.033	0.616	5.38
Co(tbzacen)	40.8	105.9	0.730	0.017	0.747	2.25
Co(tbzactn)	31.7	53.7	0.369	−0.001	0.368	−0.2
Co(tdbzmen)	−17.4	90.9	0.626	0.057	0.683	8.35
Co(acacen)	49.0	100.0	0.089	0.072	0.696	10.3

RK: 10^{-4}cm^{-1}, A_d: 10^{-4}cm^{-1}

Table VI. Cobalt-59 Spin Densities for Co(N_2S_2-Schiff Base) (LB) Complexes

	LB	PK	A_d	ρ_{3d}	ρ_{4s}	ρ_{Co}	%4s
(I)	Co(tbzacen)						
	Py	18.2	104.0	0.717	0.034	0.751	4.61
	MePy	26.0	107.7	0.742	0.030	0.772	3.83
	Pipe	18.7	107.1	0.738	0.035	0.773	4.54
	N-MeIm	29.0	112.5	0.775	0.029	0.804	3.60
	PPh_3	1.1	79.8	0.550	0.018	0.568	3.24
	PBu_3	7.9	74.5	0.513	0.029	0.542	5.28
	$P(OMe)_3$	7.6	71.5	0.493	0.027	0.520	5.27
	$P(OBu)_3$	13.5	74.5	0.513	0.024	0.537	4.47
	CO	22.1	85.1	0.589	0.022	0.611	3.62
(II)	Co(tbzactn)						
	Py	4.6	85.1	0.588	0.036	0.625	5.83
	N-MeIm	7.2	85.7	0.590	0.034	0.625	5.51
	(Pipe)	29.6	50.9	0.352	0.000	0.353	0.00
(III)	Co(tdbzmen)						
	Py	20.1	103.7	0.715	0.032	0.747	4.34
	PPh_3	2.2	75.1	0.518	0.034	0.552	6.16
	$P(OBu)_3$	1.6	66.3	0.457	0.030	0.487	6.16
	CO	21.3	67.3	0.464	0.014	0.478	2.93
(IV)	Co(tacacen)						
	Py	13.2	98.3	0.678	0.036	0.714	5.04
	CO	26.8	89.0	0.039	0.022	0.661	3.33
(V)	Co(tsalen)						
	Py	3.1	81.6	0.562	0.036	0.598	5.98

PK: $10^{-4}cm^{-1}$, A_d: $10^{-4}cm^{-1}$

Table VII. Cobalt-59 Spin Densities for Co(N_2O_2-Schiff Base) (LB) Complexes

	LB	PK	A_d	ρ_{3d}	ρ_{4s}	ρ_{Co}	%4s
(I)	Co(bzacen)						
	Py	21.9	122.6	0.845	0.040	0.885	4.50
	N-MeIm	21.7	122.0	0.841	0.040	0.881	4.51
	Pipe	24.6	124.0	0.854	0.038	0.892	4.29
	CNPy	19.6	126.3	0.869	0.043	0.912	4.75
	PPh_3	22.1	108.5	0.748	0.033	0.781	4.23
(II)	Co(salen)						
	DMF	5.4	112.8	0.777	0.049	0.826	5.89
	Py	2.4	101.5	0.699	0.046	0.745	6.14
	Py_2	27.5	113.3	0.781	0.031	0.812	3.82
	CO	16.2	102.0	0.78	0.040	0.82	
(III)	Co(salphen)						
	DMF	−9.9	103.7	0.715	0.057	0.772	7.36
	Py	5.9	105.1	0.724	0.045	0.769	5.80
	Py^2	29.6	109.9	0.757	0.028	0.785	3.57
	PPh_3	2.8	91.0	0.627	0.041	0.668	6.14
(IV)	Co(acacen)						
	Py	−5.6	88.4	0.609	0.046	0.655	7.02

PK: $10^{-4}cm^{-1}$, A_d: $10^{-4}cm^{-1}$

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REFERENCES

(1) A. L. Crumbliss and F. Basole, *J. Am. Chem. Soc.*, **92**, 55 (1970).
(2) B. M. Hoffman, D. L. Diemente, and F. Basolo, *J. Am Chem. Soc.*, **92**, 61 (1970).
(3) F. A. Walker, *J. Am. Chem. Soc.*, **92**, 4235 (1970).
(4) E. Ochiai, *J. Inorg. Nucl. Chem.*, **35**, 1727 (1973).
(5) B. M. Hoffman and D. H. Petering, *Proc, Natl. Acad. Sci. USA.*, **67**, 637 (1970).
(6) M. J. Carter, D. P. Rilleman, and F. Basolo, *J. Am. Chem. Soc.*, **96**, 392 (1974).
(7) B. B. Wayland, M. E. Abd-Elmageed, and L. F. Mehne, *Inorg. Chem.*, **14**, 1456 (1975).
(8) D. Fantucci and V. Valenti, *J. Am. Chem. Soc.*, **98**, 3832 (1976).
(9) B. S. Tovrog, D. J. Kitko, and R. S. Drago, *J. Am. Chem. Soc.*, **98**, 5144 (1976).
(10) B. M. Hoffman, F. Basolo, and D. L. Diemente, *J. Am. Chem. Soc.*, **95**, 6497 (1973).
(11) M. F. Corrigan, K. S. Murry, B. O. West, P. R. Hicks, and J. R. Pilbrow, *J. Chem. Soc. Dalton Trans.*, 1478 (1977).
(12) M. Sakurada, Y. Sasaki, M. Matsui, and T. Shigematsu, *Bull. Inst. Chem. Res., Kyoto Univ.*, **55**, 466 (1977).
(13) L. S. Chen, M. E. Koehler, B. C. Pestel, and S. C. Cummings, *J. Am. Chem. Soc.*, **100**, 7243 (1978).
(14) C. Daul, C. W. Schlapfer, and A. von Zelewsky, "Structure and Bonding 36", Springer-Verlag, Berlin, Heidelberg, New York, 1979, p. 129.
(15) W. C. Lin, *Inorg. Chem.*, **15**, 1114 (1976).
(16) F. Cariati, D. Galizzioli, F. Morazzoni, and C. Busetto, *J. Chem. Soc. Dalton Trans.*, 556 (1975).
(17) A. von Zelewsky and H. Fierz, *Helv. Chim. Acta*, **56**, 977 (1973).
(18) M. A. Hitchman, *Inorg. Chem.*, **16**, 1985 (1977).
(19) V. Malatesta and B. R. McGarvey, *Can. J. Chem.*, **53**, 3791 (1975).
(20) C. Busetto, F. Cariati, A. Fusi, M. Gullotti, A. Pasini, F. Morazzoni, R. Ugo, and V. Valenti, *J. Chem. Soc. Dalton Trans.*, 754 (1973).
(21) F. L. Urbach, R. D. Berman, H. A. Topich, M. Hariharan, and B. J. Kalbacher, *J. Am. Chem. Soc.*, **96**, 5063 (1974).
(22) F. Cariati, F. Morazzoni, C. Busetto, G. D. Piero, and A. Zazzetta, *J. Chem. Soc. Dalton Trans.*, 342 (1976).
(23) M. Sakurada, Y. Sasaki, M. Matsui, and T. Shigematsu, *Bull. Chem. Soc. Japan*, **52**, 1861 (1979).
(24) R. H. Bailes and M. Calvin, *J. Am. Chem. Soc.*, **69**, 1886 (1947).
(25) A. E. Martell, R. L. Belford, and M. Calvin, *J. Inorg. Nucl. Chem.*, **5**, 170 (1958).
(26) P. R. Blum, R. M. C. Wei, and S. C. Cummings, *Inorg. Chem.*, **13**, 450 (1974).
(27) H. Behringer and A. Grimm, *Liebigs Ann. Chem.*, **682**, 188 (1965).
(28) S. C. Tang, S. Koch, G. N. Weinstein, R. W. Lane, and R. H. Holm, *Inorg. Chem.*, **12**, 2589 (1973).
(29) B. R. McGarvey, *J. Phys. Chem.*, **71**, 51 (1967).
(30) B. T. Tovrog and R. S. Drago, *J. Am. Chem. Soc.*, **96**, 6765 (1974).
(31) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Am. Chem. Soc.*, **86**, 4508 (1964).
(32) B. R. McGarvey, *Can. J. Chem.*, **53**, 2498 (1975).
(33) L. M. Engelhardt, J. D. Duncen, and M. Green, *Inorg. Nucl. Chem. Letters*, **8**, 735 (1972).
(34) M. C. R. Symons and J. G. Wilkinson, *J. Chem. Soc., A*, 2069 (1971).